Russian Chemical Bulletin, International Edition, Vol. 60, No. 11, pp. 2175—2179, November, 2011

The reaction energies of ethylene, CO, and N_2 with proton, hydrogen atom, and hydride ion*

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It is shown by quantum chemical simulation (MP2/aug-cc-pVTZ) that the energy of addition of H^+, $H^{\cdot}$, and H^- decreases in the order ethylene, CO, and N_2. The energies of additions of CF_4, dimethyl ether, and BF_3 to the ions and radicals formed were calculated. Unlike the $CH_3CH_2^-$ ion, the HCO^- ion can add exothermically not one, but two BF_3 molecules.

Key words: quantum chemical calculations, MP2 method, multiple bonds, protonation, hydrogen atom, hydride ion, ethyl cation.

Ethylene, CO, and N_2 are important substrates of the modern industry. The reactions of these compounds with hydrogen underlay the production of many chemical products and semiproducts of "big" chemistry. Despite the multiyear investigations, the mechanistic details of these industrial processes are still unclear. It is assumed that the acid-catalyzed reactions of alkenes involve the protonation of the substrate molecules.[1] The reactions of alkenes involving free radicals[2] and alkene polymerization initiated by anions[3] are well known. In these reactions, a free or coordinated alkene is thought to be attacked by a free radical or coordinated negatively charged particle (the hydride ion in the case of hydroformylation). At the same time, the free ethylene is inactive towards the hydroxide anion. On the contrary, carbon monoxide reacts with both the OH^- and methoxide anions.[4] The formyl radical is considered as a possible intermediate in the low-temperature oxidation of CO. A low energy of the H—CO bond (16 kcal mol^{-1}) allows one to assume that under the burning conditions, this radical is not a long-lived particle and disappears due to direct decomposition.[5]

In the present work, we estimated the reaction energies of $H^{\cdot}$, H^+, and H^- with the molecules containing multiple bonds (C=O, $CH_2=CH_2$, and N≡N) by quantum chemical simulation.

Methods of Calculation

Geometry optimization and calculations of vibrational frequencies were performed using the GAMESS-US program package.[6] The Hartree—Fock (HF) approximation with the second-order corrections of the Möller—Plesset perturbation theory (MP2) served as the main calculation method. The aug-cc-pVTZ triexponential correlation-consistent basis set was used for all atoms.[7,8]

The adequacy of the method selected is evidenced by a good agreement of the calculated parameters with experimental data and higher-level calculation data. The maximum discrepancy between the calculated bond lengths and literature data is not more than 0.01 Å.

Results and Discussion

Proton addition. All calculation methods that were used showed that the addition of the H^+ cation to all above-mentioned molecules affords equilibrium structures. All addition reactions lead to the decrease in the total system energy. The proton addition to the ethylene molecule without considering the influence of other particles affords only one equilibrium bridging structure with the symmetric arrangement of the H atoms in the plane of the C=C multiple bond (**1**, Fig. 1), which agrees with the experimental and calculated data for the gaseous phase.[9a—c]

Note that as in the ethylene molecule, in the diborane molecule, which can be regarded as the double protonated dianion $B_2H_4^{2-}$, four terminal H atoms are in one plane and two bridging H* atoms are above and under this plane. In other words, the bridging C—H*—C fragments is identical to the B—H*—B bridge in the diborane molecule (the bond lengths: C—H* is 1.308 Å and B—H* is 1.310 Å).

The ability of light elements, in particular, proton, to afford π-complexes was a matter of controversy for a long

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* Dedicated to the Academician of the Russian Academy of Sciences O. M. Nefedov on occassion of his 80th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2133—2137, November, 2011.

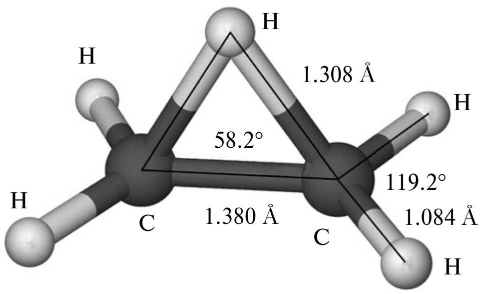

Fig. 1. Addition of proton to the ethylene molecule (structure **1**).

time. It was thought that the symmetric carbenium ions can arise only in the case of d-elements, which can form not only the π-acceptor, but also donor bond. Our results confirm the hypothesis of existence of symmetric carbenium ions with cations incapable of dative interaction with the antibonding π*-orbital of the ligand. Certainly, for the formation of such π-complex, the fact that a complexation agent could eliminate readily the ligands, *e.g.*, water molecules replaced by the ethylene molecules, is of significance.

It should be noted that the potential energy surface (PES) has a stationary point with one imaginary frequency corresponding to the vibrationally excited classic $CH_3CH_2^+$ cation with the energy, which is by 6 kcal mol^{-1} higher than that of structure **1** (see Ref. 9).

The proton transfer from the H_3^+ ion to the CO molecule has been studied in a series of works.[10] Our calculations showed that upon the reaction of CO with H^+, two ions with linear equilibrium structures arise, the proton being localized near to the C atom in one of these ions and near to the O atom in another one (Tables 1 and 2). The geometry parameters obtained coincide with both higher-level calculation data[11—13] and experimental data.[14—16] The energy of the H—CO$^+$ is by ~46 kcal mol^{-1} lower than that of the isomer CO—H$^+$. No equilibrium configuration corresponding to the π-coordination of proton was found.

The acid-catalyzed reactions of the N_2 molecule are unknown. However, the transfer of the cationoid particle $O^{\delta+}$ from the oxygenyl vanadium(v) complex to the N_2 molecule has been observed in the reaction of N_2 with the vanadium(v) complex in trifluoroacetic acid.[17] In this context, the estimation of the proton affinity of the N_2 molecule and geometry of the protonated molecule was of interest. The calculations showed that the protonated form N_2H^+ is analogous to the linear structures H—CO$^+$ and CO—H$^+$.

The proton affinity (Table 3) decreases in the order $CH_2{=}CH_2$ > C=O(@C) > N≡N > C=O(@O)*. Unexpectedly, it was found that the protonation energy for CO at the O atom is less than that for N_2.

Table 1. The CO and CH bond lengths (*R*), the O—C—H angle (α), and relative total energies (*E*) of the structures HCO^+, HCO, and HCO^-

Method	R_{CO}	R_{CH}	α/deg	*E* /kcal mol^{-1}
	Å			
HCO^+				
MP2/ aug-cc-pVTZ	1.1192	1.0911	180.0	0
CCSD(T)/ aug-cc-pV5Z[13]	1.1069	1.0936	180.0	−33.62
Experiment[14]	1.1047	1.0972	180.0	—
HCO				
UMP2/ aug-cc-pVTZ	1.1831	1.1161	124.1	−180.92
RCCSD(T)/ aug-cc-pV5Z[13]	1.1768	1.1192	124.6	−219.13
Experiment[15]	1.177	1.1550	123.0	—
HCO^-				
MP2/ aug-cc-pVTZ	1.2461	1.2032	109.7	−184.08
CCSD(T)/ aug-cc-pV5Z[13]	1.2381	1.2162	109.8	−224.90
Experiment[16]	1.25±0.05	1.210±0.02	109.0±2	—

Note. The total energy of the structure HCO^+ is equal to −113.380367 a.u.

Table 2. The CO and OH bond lengths (*R*), the C—O—H angle(α´), and relative total energies (*E*) of the structures COH^+, COH, and COH^-

Method	R_{CO}	R_{CH}	α´ /deg	*E* /kcal mol^{-1}
	Å			
COH^+				
MP2/aug-cc-pVTZ	1.1594	0.9953	180.0	0
CCSD(T)/ aug-cc-pVQZ[11]	1.1553	0.9891	180.0	−37.00
COH				
UMP2/ aug-cc-pVTZ	1.2795	0.9791	112.3	−181.96
RCCSD(T)/ aug-cc-pV5Z[12]	1.2742	0.9755	112.9	−253.26
COH^- (triplet)				
UMP2/aug-cc-pVTZ	1.2655	1.0055	115.2	−172.63

Note. The total energy of the structure COH^+ is equal to −113.30670 a.u.

As expected, the addition of $(CH_3)_2O$ to structure **1** is accompanied by a significant heat effect (53.1 kcal mol^{-1})

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* The symbols (@C) and (@O) designate the proton localization positions in the protonated CO molecule .

Table 3. The formation energies of the addition reaction products $A + H^+ \rightarrow AH^+$ (*1*), $A + H \rightarrow AH$ (*2*), $A + H^- \rightarrow AH^-$ (*3*) in view of zero-point energies (ZPE)

Method	D_0/kcal mol^{-1} for reactions		
	1	*2*	*3*
		$A = C_2H_4$	
MP2/aug-cc-pVTZ	161.74	31.69	17.86[a]
Experiment	162.6[18]	28.7±0.2[19]	—[b]
		A = CO (@C)	
MP2/aug-cc-pVTZ	143.74	11.34	6.10
(R)CCSD(T)/ aug-cc-pV5Z[13]	140.26	14.04	4.52
Experiment	142.0[18]	13.9 (14.3)[20]	5.2±0.2
		A = CO (@O)	
MP2/aug-cc-pVTZ	99.3	−34.3	−52.95[c]
		$A = N_2$	
MP2/aug-cc-pVTZ	116.2	−23.5	—
Experiment[18]	118.0	—	—

[a] The value $D_e = 17.33$ kcal mol^{-1} was obtained for $H_3CCH_2^-$ by the CCSD(T)/aug-cc-pVTZ method (without regard to the zero-point energy). [b] Not available. [c] The UMP2/aug-cc-pVTZ calculation of the triplet state of CO—H^-.

and isomerization of the π-complex to the classic carbocation to result in the formation of dimethylethyloxonium. Unexpectedly, isomerization of the π-complex to the ethyl carbocation with a heat effect of 1.9 kcal mol^{-1} occurs even in the reaction of structure **1** with CF_4. In the adduct of the classic ethyl cation with CF_4, the contact C...F is 2.197 Å, which suggests the absence of the chemical bond. Transformation of the nonclassical cation to the classic form under the action of the CF_4 molecule, which reacts very weakely with the carbenium ion and is chemically inert in ionic reactions, excludes virtually the existence of the nonclassical cation **1** in the condensed phase. This result puts in doubt the mechanisms of liquid-phase reactions including the step of the π-complex formation in the acid-catalyzed transformations of ethylene.[21,22]

The proton affinity of dimethyl ether is by 40 kcal mol^{-1} higher[23] than the maximum value for CO. Consequently, the approach of the protonated CO molecule with dimethyl ether results necessarily in the deprotonation of the H—CO^+ cation.

Addition of the hydrogen atom. The addition of $H^\bullet$ to all above-mentioned molecules affords equilibrium structures. All addition reactions lead to a decrease in the total system energy. The addition energy decreases in the order $CH_2{=}CH_2 > C{=}O > N{\equiv}N$.

The $H^\bullet$ radical adds exothermically to ethylene to form only the classic $CH_3CH_2^\bullet$ radical. The adduct of $H^\bullet$ and CO represents the structure H—$CO^\bullet$ (see Table 1).

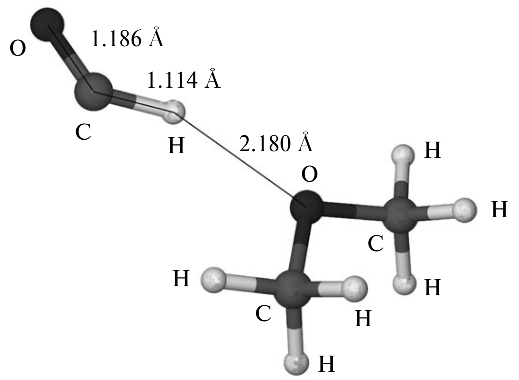

Fig. 2. Addition of the CO—$H^\bullet$ radical to the dimethyl ether molecule.

There are also minima on PES corresponding to the alternative structure CO—$H^\bullet$ and addition product of $H^\bullet$ to N_2; however, their formations require energy consumption (see Table 3). Note that upon kinetic study of the reaction

$$H{-}CO^\bullet + IM \longrightarrow H^\bullet + CO + IM,$$

among others molecular nitrogen was used as the inert media (IM).[5]

In contrast to the carbenium ion $CH_3CH_2^+$, the $CH_3CH_2^\bullet$ radical does not form new compounds with dimethyl ether. The CO—$H^\bullet$ radical in contrast to the CO—H^+ cation adds to dimethyl ether through a weak (3.6 kcal mol^{-1}) hydrogen bond (Fig. 2). One can conclude that dimethyl ether makes no significant contribution to stabilization of the radicals.

Addition of the hydride anion. It is thought that the H^- ion plays an important role in the processes proceeding in the interstellar space.[24] Numerous reactions of alkenes and CO with hydride ion donors are known. There seemed that the Vol´pin—Shur reaction (nitrogen fixation in the reactions with organometallic compounds under mild conditions[25]) involves the hydride ion transfer to the free or coordinated N_2 molecule. It was found unexpectedly that in contrast to the addition of H^+ and $H^\bullet$, the N_2 molecule forms no equilibrium structure with the hydride ion. The formation energy of the addition products of hydride ion decreases in the order CH_2CH_2—H^- > H—CO^- > CO—H^- (see Table 3), the energy for CO—H^- is given in the triplet state.*

The possible influence of acids or acid vacancies on the solid surface on these reactions was simulated just qualitatively by the addition of BF_3 to anions. Note that two adducts with the B—O and B—C bonds were found for H—CO^-. The formation energy of the adducts of

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* No singlet state with closed electron shells was found. The calculation of hypothetic singlet state with opened electron shells requires the use of multiconfiguration methods.

BF_3 with $CH_3CH_2^-$ and H—CO$^-$ decreases in the order BF_3—CH_2CH_2—H$^-$ > BF_3—C(H)O$^-$ > HCO$^-$—BF_3.

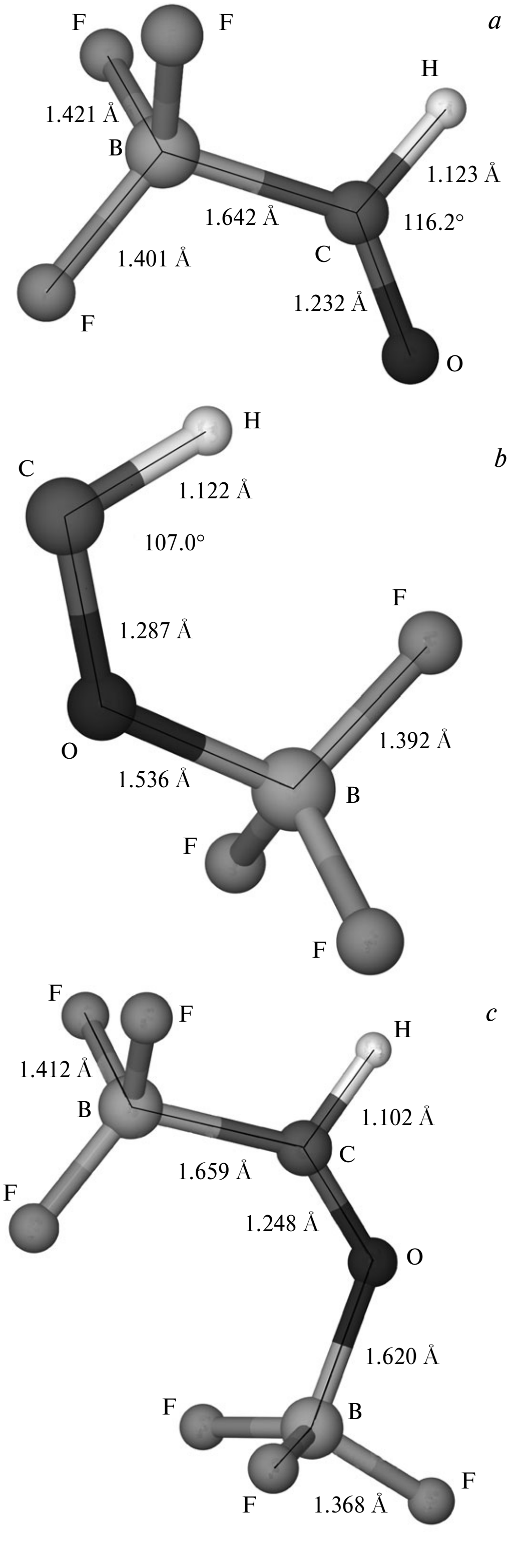

Fig. 3. Addition of the BF_3 molecules to the HCO$^-$anion: adduct of HCO$^-$ and BF_3(@C) (*a*), adduct of HCO$^-$ and BF_3 (@O) (*b*), adduct of HCO$^-$ with two BF_3 molecules (*c*).

The calculations showed that not only one, but also two BF_3 molecules can add exothermically to H—CO$^-$ (Fig. 3) and only one BF_3 molecule can add exothermically to the carbanion $CH_2CH_3^-$ (Fig. 4). The comparison of energies for the overall reactions

$$\mathrm{C{=}O + H^- + BF_3 \longrightarrow BF_3{-}C(H)O^-},$$

ΔE = 86 kcal mol^{-1},

$$\mathrm{C{=}O + H^- + 2\,BF_3 \longrightarrow BF_3{-}C(H)O^-{-}BF_3},$$

ΔE = 111 kcal mol^{-1},

$$\mathrm{CH_2{=}CH_2 + H^- + BF_3 \longrightarrow BF_3{-}CH_2CH_2{-}H^-},$$

ΔE = 110 kcal mol^{-1},

shows that with increase in the number of acidic sites, the reactivities of the CO and ethylene molecules become comparable. It is possible that the hydride ion transfer with stabilization of the resulted adduct requires participation of more than one acidic site. This is provided on heterogeneous hydrogenation catalysts being applied usually to a Lewis-acid support and having own acidic sites.

For sure, our attempt to estimate the reactions of important chemical substrates in terms of energetics should not be considered as a complete analysis of possible reaction pathways of these compounds. The effects of catalysts and solvents were not taken into account in a proper way. Nevertheless, some results obtained seem to be not

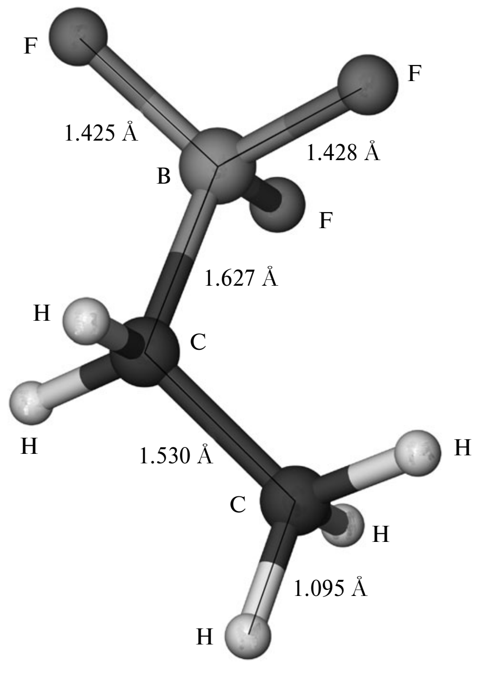

Fig. 4. Adduct of $CH_2CH_3^-$ and BF_3.

only unexpected, but also fruitful for further studies of industrially important processes.

This work was financially supported by the Russian Academy of Sciences (Program No. 01 of the Department of Chemistry and Material Sciences "Theoretical and experimental studies of the nature of chemical bond and mechanisms of the most important chemical reactions and processes").

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Received May 23, 2011;
in revised form October 20, 2011